

dispersion effects for cesium and a number of other heavy atoms at the  $L_{III}$  absorption edge (Phillips, Templeton, Templeton & Hodgson, 1978), the virtue of taking advantage of even small effects in anomalous dispersion (Hendrickson & Teeter, 1981) and apparatus for making simultaneous measurements of anomalous dispersion over a range of wavelengths (Arndt, Greenhough, Helliwell, Howard, Rule & Thompson, 1982), combined with the advancing theoretical results, will provide a broad range of opportunities to test and develop optimal procedures.

I am very grateful to Mr Stephen Brenner for making the computations reported here.

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## The Symmetry of Convergent-Beam Electron Diffraction Patterns from Bicrystals

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### Abstract

A discussion of the relationship between the symmetry of bicrystals and the resulting symmetry of convergent-beam electron diffraction (CBED) patterns is presented. For this purpose bicrystal symmetry is defined from the symmetry of the dichromatic pattern or complex formed by the interpenetrating lattices or structures of the individual crystals in a bicrystal. The interrelation between the possible coloured point groups and the diffraction groups, characterizing the symmetry of a CBED pattern, is established. These results are illustrated by a determination of the symmetry of thin twinned Au crystals from suitable CBED patterns. These experiments give information about the state of relative translation of the two crystals at the grain boundary and are consistent with the state of zero translation expected for a (111) coherent twin

boundary in Au. It is pointed out that the interpretation of the CBED pattern symmetry may be complicated by a non-ideal location of the boundary plane in a bicrystal.

### 1. Introduction

It is now well established that the symmetry of single crystals may be determined in a reliable manner using the technique of convergent-beam electron diffraction (CBED). The relation between the symmetry of CBED patterns and crystal symmetry has been discussed by several authors (Goodman, 1975; Tinnappel, 1975; Buxton, Eades, Steeds & Rackham, 1976). In particular, Buxton *et al.* (1976) have presented a systematic classification of the symmetry of CBED patterns in terms of 31 diffraction groups, which is a very useful tool for crystal symmetry determination.

This paper is concerned with the application of

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CBED to bicrystals in the form of thin platelets with the boundary plane assumed to be coincident with the mid-plane of the specimen. As has been pointed out briefly elsewhere (Schapink & Mertens, 1981), it is possible with this specimen geometry to draw conclusions about the state of translation of the crystals at the boundary plane from a determination of the symmetry of the bicrystal using CBED. In order to explore this method in a more detailed manner an extension of the method of Buxton *et al.* (1976) to bicrystal symmetry is presented here in which the bicrystal symmetry is described by using the dichromatic patterns. The concept not only simplifies consideration of the retention or destruction of bicrystal symmetry elements due to relative displacements of the two crystals (Pond & Bollmann, 1979), it also simplifies the derivation of the diffraction symmetry, for example when the projection is made (§ 2.3). The method will be illustrated by the results of the symmetry determination of a number of thin twinned Au crystals employing the CBED technique.

## 2. CBED pattern symmetry from bicrystals

### 2.1. The dichromatic description of bicrystal symmetry

As mentioned in the *Introduction*, the bicrystal symmetry is described by using the concept of differently coloured (*e.g.* black and white) interpenetrating lattices introduced by Pond & Bollmann (1979). In general, there is a basis associated with each lattice, a white basis made up of 'white atoms' with the white lattice and a black basis of 'black atoms' with the black lattice so that strictly speaking, in the sense of Pond & Vlachavas (1983), the symmetry required is that of the dichromatic complex III (*c*). This is the symmetry generated by the relative orientation and position of the two crystal structures – if only their lattices were considered or if the crystals were holosymmetric as for the twinned Au crystals investigated in detail below (§ 3), the symmetry would be that of the dichromatic pattern as originally described by Pond & Bollmann (1979). In either case, however, the important point is that the symmetry of the dichromatic complex or pattern depends on the relative positions of the crystals so that by, for example, using CBED to obtain the dichromatic symmetry, we obtain information about the relative displacement of the crystals. A table showing the possible symmetries associated with a first-order twin boundary in a holosymmetric f.c.c. crystal that will be used later in our investigation of the twinned Au crystals has been given by Schapink & Mertens (1981). In particular, it can be seen from this table that the dichromatic point symmetry may be modified by a translation of one crystal with respect to the other making this technique particularly convenient for convergent-beam diffraction work.

However, in order to see the dichromatic symmetry in a convergent-beam pattern, an appropriate specimen that displays any symmetry relation between the crystal components is required. The ideal specimen is therefore constructed by cross-sectioning the dichromatic complex (or pattern) (Pond & Vlachavas, 1983) on a plane perpendicular to the chosen zone axis\* and removing all the 'black' atoms above this plane and all the 'white' atoms below, as in Fig. 1. In order to preserve any symmetry relation between the upper and lower parts of the bicrystal so created, the interface should also be the mid-plane of the sample as pointed out by Schapink & Mertens (1981). Although this may seem rather specialized it is just the analogue for electron diffraction of the rule in X-ray diffraction that the twin law is only apparent as a symmetry of the composite if the twins are equally developed (Buerger, 1960, p. 58).

According to Pond & Bollmann (1979) and Pond & Vlachavas (1983), the spatial symmetry of the dichromatic pattern or complex may have any dimensionality from zero to three depending on the number of non-collinear translation axes there are. Here, we shall only be concerned with the three-dimensional case, that is, for those relative orientations of the component crystals for which a 3D coincidence site lattice (CSL) exists.† The symmetry of the dichromatic complex is thus described by one of the Shubnikov space groups and its point group by one of the Shubnikov point groups. There are 90 of these coloured point groups (see, for example, Shubnikov & Belov, 1964;

\* Perpendicular to the zone axis if the symmetric Laue condition is satisfied: more strictly, in the asymmetric Laue case, it must be sectioned on a plane parallel to the foil as in Fig. 1.

† But note that relative translation of the lattices may modify the CSL: see Grimmer, Bollmann & Warrington (1974).

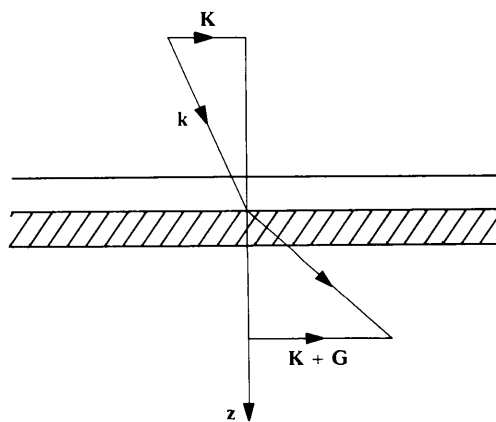


Fig. 1. Schematic representation of the idealized diffraction experiment. The bicrystal is formed by removing all the 'black' atoms above and the 'white' atoms below the mid-plane of the sample. Electrons incident in direction  $K$  are diffracted into direction  $K + G$ .

Opechowski & Guccione, 1965), of which 32 are grey groups that are useful for describing the symmetry of stacking-fault or inversion boundaries (Pond & Vlachavas, 1983). The grey groups will not be considered here, nor will the ordinary monochromatic point groups which can be used to describe the symmetry of bicrystals with an interphase boundary where the two components are different. The remaining 58 coloured groups describe the symmetry of bicrystals with a special orientation relationship between the components such as occurs in twins, for example. We shall further restrict ourselves to twins where  $\Sigma$ , the ratio of the volume of the unit cell of the CSL to that of the crystal lattice, is greater than one so that twinning by merohedry is excluded [ $\Sigma$  may be regarded as the twin index in the definition of Friedel (1926)]. It is readily found that the number of coloured point groups for this type of bicrystal is reduced from 58 to 34 since such a point group can neither belong to any of the six point groups associated with the cubic system nor contain a coloured inversion centre, thus eliminating 18 of the remaining point groups.

## 2.2. Diffraction from bicrystals

In order to establish the connection between the 34 remaining coloured point groups and the 31 diffraction groups we proceed as in Buxton *et al.* (1976), hereafter referred to as I. We imagine that the incident beam impinges on a thin bicrystal specimen constructed as in § 2.1 with flat parallel surfaces so that electrons incident in direction  $\mathbf{K}$  are diffracted into  $\mathbf{K} + \mathbf{G}$  (Fig. 1) where  $\mathbf{K}$  and  $\mathbf{G}$  stand for the components of the electron wavevector  $\mathbf{k}$  and reciprocal-lattice vector  $\mathbf{g}$ , respectively, that are perpendicular to  $\mathbf{z}$  as in I. Then, if a transformation  $S$  represented by the Seitz symbol  $\{R|\mathbf{v}\}$  (Seitz, 1936) is a symmetry of the system, *i.e.* of the bicrystal including the interface, it follows from the invariance of the Hamiltonian of the fast electrons that

$$S(\Psi_{\mathbf{k}}) = \Psi_{R\mathbf{k}} \quad (1)$$

to within a phase factor which depends on  $\mathbf{v}$ , the translational part of  $S$ . Equation (1) shows that the wavefunction  $\Psi_{\mathbf{k}}$  for electrons incident in direction  $\mathbf{k}$  is related to that for the electrons incident in direction  $R\mathbf{k}$ , where  $R$  is the rotational part of the transformation  $S$ . The symmetry relations between the diffracted beams that define the diffraction groups are obtained from (1) as in I, either directly if  $R$  leaves the electron beam incident on the specimen from above as in Fig. 1, or indirectly using the reciprocity relation (Pogany & Turner, 1968; Buxton *et al.*, 1976) if electrons in direction  $R\mathbf{k}$  are incident on the specimen from below. As usual, relations of the second kind are indicated by a subscript  $R$  (for Reciprocity) in the diffraction group.

In general, the elements  $S$  of the symmetry group of the bicrystal may be obtained from the dichromatic

complex III (c) by cross-sectioning as described in § 2.1 or by Pond & Vlachavas (1983). Here, however, we are only interested in point symmetries so we need only consider the dichromatic point group. The symmetry operations required are those that leave the bicrystal sketched in Fig. 1 invariant, *i.e.* vertical ordinary operations that leave the  $z$  axis unchanged and horizontal coloured operations that transform  $z$  into  $-z$ . The latter therefore only appear in the diffraction group by virtue of the reciprocity relation, *i.e.* as an ' $R$ ' operation.

As an example, consider the  $\Sigma = 3$  CSL for the first-order twin boundary in Au. According to Schapink & Mertens (1981), if there is no translation of the white crystal with respect to the black, the point group is  $6'/m'm'm$  with the hexad axis parallel to  $[111]$ . As usual, we use a prime to denote an antisymmetric or 'coloured' operation that turns a 'white' atom into a 'black' one. If we prepare a sample for taking a  $[111]$  convergent-beam pattern, the dichromatic group has to be sectioned on  $(111)$ , leaving only an ordinary triad axis, the three ordinary vertical mirrors, the coloured horizontal mirror and three coloured horizontal diad axes making up the symmetry group  $\bar{6}'m2'$  [the point group of the bicrystal III (b) in the terminology of Pond & Vlachavas (1983)]. At this stage, the prime for the antisymmetry serves only to remind us that the operation connects the two crystal components but otherwise has no further physical significance and can be ignored. The point symmetry of the bicrystal is therefore  $\bar{6}m2$  and its diffraction group  $3m1_R$  as in I.

The complete list of the diffraction groups that may occur for different cross sections of each of the 34 coloured point groups of interest here is given in Table 1. This is analogous to Table 3 of I, but note that it contains point groups differing only by the distribution of primes over the symmetry elements as these are quite distinct and often lead to very different diffraction groups. An example is shown in Fig. 2 where we give the diffraction group as seen down  $[001]$  for the family of coloured point groups belonging to  $42m$ . It should also be noted that, as mentioned above, ' $R$ ' operations only occur in the diffraction group due to coloured symmetry operations in the dichromatic point group that relate one crystal component to the other. Thus, if we were to encounter a bicrystal with a state of translation at the boundary such that the resulting point group contains only ordinary symmetry elements, the diffraction group would be one of the ten which do not contain the symbol  $R$ . A similar result would be obtained for a bicrystal with an interphase boundary.

## 2.3. The effect of the projection approximation on bicrystal diffraction symmetry

For low-index zone axes it frequently happens for reflexions near the origin that either the projection



means that additional information about the dichromatic group is available. For example, diffraction group  $3m1_R$  can only occur in combination with  $6mm1_R$  in the projection approximation if the dichromatic group is  $6'/m'm'm$  seen down its  $[00.1]$  axis. Table 1 therefore also lists the possible diffraction groups that can occur in the projection approximation for each of the 34 dichromatic groups considered here.

#### 2.4. State of translation at the boundary

It has been found in recent years that a grain boundary in a bicrystal is frequently characterized by a rigid translation away from the coincidence position of the constituent crystals. There is both limited experimental evidence for this type of relaxation at the boundary (mainly restricted to boundaries belonging to the  $\Sigma = 3$  system in f.c.c. metals and materials having the diamond structure) as well as evidence from computer simulation of the equilibrium position of atoms in a boundary (Vitek, Sutton, Smith & Pond, 1980).

For diffraction purposes, the symmetry of bicrystals may be conveniently classified using the dichromatic groups as we have just seen, but the important point is that relaxation at the boundary leading to a rigid translation generally produces a change in the dichromatic pattern symmetry (Pond & Bollmann, 1979; Schapink & Mertens, 1981). Consequently, by determining the dichromatic pattern symmetry we can often draw conclusions about the state of translation at a particular boundary in a bicrystal. This aspect is emphasized in this paper for the particular bicrystal geometry in which the boundary is the mid-plane of the specimen. Although as pointed out in § 1 this is analogous to the situation in X-ray diffraction, such an idealized geometry may be difficult to obtain experimentally, especially if determining the dichromatic point group using Table 1 requires convergent-beam patterns from several zone axes. However, we expect that small deviations from the ideal geometry will not greatly influence the results, as is usually found in single-crystal CBED work.

Finally, it should also be pointed out that knowledge of the dichromatic point group is not always sufficient to determine the state of translation in a bicrystal. For bicrystals based on holosymmetric f.c.c. or b.c.c. crystals the possible dichromatic pattern symmetries for different types of CSL boundaries and different states of translation of a particular boundary have been tabulated (Pond & Bollmann, 1979; Schapink & Mertens, 1981). From this work it is clear that in some cases the full space-group symmetry is needed in order to determine the type of translation existing at a boundary. The latter symmetry should be obtained in the usual way by considering extinctions due to screw axes or glide planes (Gjønnnes & Moodie, 1965; Goodman, 1978; Steeds & Vincent, 1983).

### 3. Experimental results

As an illustration of the method presented in the previous section we now discuss the symmetry determination of a number of twinned Au crystals. Thin electron-transparent Au single crystals with a  $[111]$  surface normal were obtained using a method described previously (Erlings & Schapink, 1978). Occasionally, these crystals were found to contain a coherent twin boundary parallel to the surface. The presence of a twin boundary was established using standard selected-area diffraction patterns taken at a suitable axis, e.g. a  $\langle 123 \rangle$  axis. It should be noted, however, that in this way no decision can be made as to whether the number of twin boundaries parallel to the surface equals 1 or is larger than 1. This uncertainty may have some influence on the details of the CBED patterns to be discussed below.

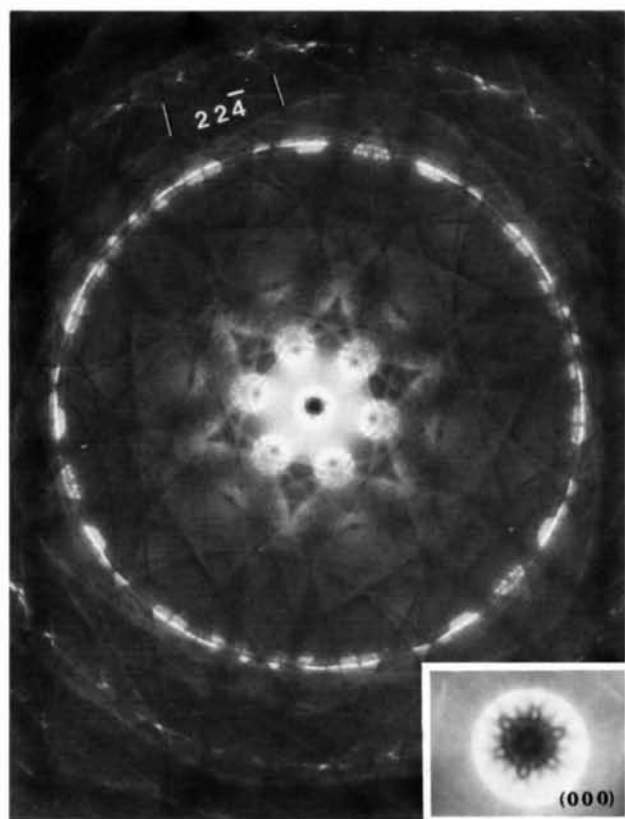
All CBED patterns in this investigation were obtained with a Philips EM-400T electron microscope operating at 100 kV in the STEM mode. Care was taken to avoid areas in the crystals in which local defects could have altered the resulting pattern symmetry. In order to reduce diffuse scattering the specimens were cooled to liquid-nitrogen temperature.

As has been pointed out elsewhere (Schapink & Mertens, 1981), a twinned f.c.c. crystal containing a coherent twin boundary is expected to belong to the point group  $6'/m'm'm$ . This is because the rigid translation of the crystals at the boundary is expected to be zero for a  $(111)$  coherent twin boundary. According to Table 1 and as discussed in § 2.2, this point group leads to diffraction group  $3m1_R$ . Fig. 3 shows a  $[111]$  zone-axis pattern for a twinned Au crystal, together with details from the  $(000)$  bright-field disc. The latter has  $6mm$  symmetry as also may the low-order zero layer  $220$  reflexions, but the symmetry of the whole pattern is clearly only  $3m$  because the bright ring of first-order Laue-zone reflexions does not possess mirror symmetry parallel to the  $224$  Kikuchi bands. Reference to Table 2 of I shows that the diffraction group is therefore  $3m1_R$  and hence from Table 1 that the dichromatic point group is either  $6'/m'm'm$  or  $\bar{6}'m2'$ . For comparison, the  $3m$  symmetry of the corresponding whole pattern and  $(000)$  disc from a Au single crystal seen down  $[111]$  which has diffraction group  $6_Rmm_R$  is displayed in Fig. 4(a).

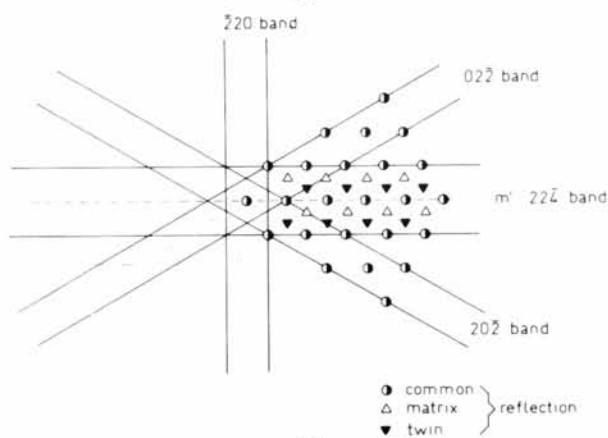
The dichromatic group  $\bar{6}'m2'$  would imply an arbitrary translation in the  $z$  direction along the common  $[111]$  axis of the crystals (Schapink & Mertens, 1981), which is unlikely for a coherent twin boundary in Au, but we can dismiss this alternative dichromatic point group by CBED by looking at the internal symmetry of a  $220$  dark-field reflexion in the Bragg condition (Fig. 5). This appears to have  $2mm$  symmetry, which does not accord with what we should expect for diffraction group  $3m1_R$  as the only special

reflexions displaying  $2mm$  symmetry in this diffraction group are those lying on the lines of mirror symmetry in the group, *i.e.*  $22\bar{4}$  reflexions *etc.* The  $220$  reflexion should only display the same internal symmetry as any

general reflexion, *i.e.* 2 according to Table 2 of I. However, these low-order zero-layer reflexions do not show any evidence of three-dimensional diffraction effects unlike those taken from single-crystal gold specimens (Fig. 4*b*), so we may apply the projection approximation to them. As described in § 2.3 and shown in Table 1, the relevant diffraction group from  $6'/m'm'm$  is then  $6mm1_R$  for which *both* the  $220$  and

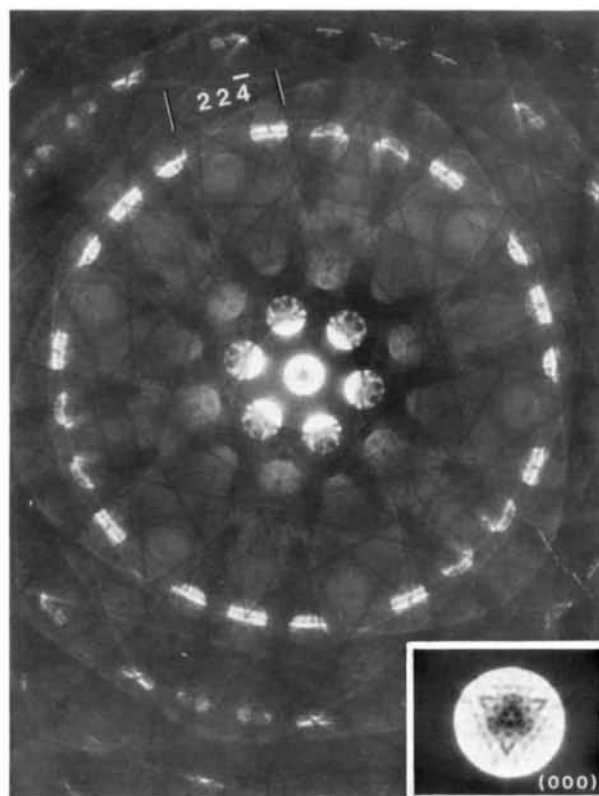


(a)

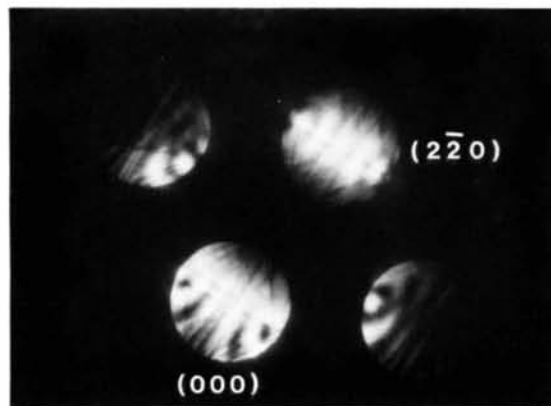


(b)

Fig. 3. (a)  $[111]$  zone-axis pattern of a twinned Au bicrystal; the inset shows details of the  $(000)$  bright-field disc. (b) Schematic drawing of part of the zero and first layer of the reciprocal lattice of a twinned f.c.c. crystal close to the  $[111]$  orientation. For clarity the location of reflexions in the second layer has not been included; these can, however, easily be obtained by interchanging the positions of the black and white triangles of the first layer.



(a)



(b)

Fig. 4. (a)  $[111]$  zone axis of a Au single crystal; the inset shows details of the  $(000)$  disc. (b)  $(220)$  disc from a Au single crystal in Bragg position. The fine high order Laue-zone lines have no symmetry.

224 reflexions should have  $2mm$  internal dark-field symmetry. For  $6'm2'$ , on the other hand, the projection diffraction group is still  $3m1_R$ , which cannot account for the internal dark-field symmetry. The dichromatic point group is therefore  $6'/m'm'm$ .

With this group, it is also easy to explain the  $6mm$  symmetry of the six low-order layer 220 reflexions in Fig. 3 that we noted earlier by invoking the projection approximation when the vertical coloured mirror parallel to  $(2\bar{2}0)$  acts as an ordinary mirror. In fact, it continues to act as an ordinary mirror for the low-order zero-layer reflexions even when we tilt further along the 224 Kikuchi band as in Fig. 6. However, it is apparent from the lack of symmetry between the higher-order pairs of matrix/twin reflexions such as the 551 reflexions arrowed in Fig. 6 (the disposition of matrix and twin reflexions is shown in Fig. 3*b*) and from the Kikuchi pattern itself, especially when we tilt further along the 224 band, Fig. 7, that it cannot be a true mirror symmetry of the diffraction group. It may also be noted in passing that the Kikuchi pattern always shows the symmetry we should expect for the diffraction group, indicating that the reciprocity relation holds for electrons that have been diffusely or inelastically scattered as well as for those that have only undergone coherent elastic scattering (Pogany & Turner, 1968).

In a number of twinned Au crystals encountered in this investigation several details of the patterns observed deviated from those shown in Figs. 3, 6 and 7. Such deviations are primarily attributed to the location of the boundary plane in the crystal, *i.e.* the boundary deviates from the mid-plane position by a sufficiently large fraction of the relevant extinction distances to affect the amplitudes of the diffracted waves appreciably. It is also possible that the number of twin boundaries parallel to the surface in some crystals was greater than one. It might be best to study the effect of the position of the boundary on the symmetry of a

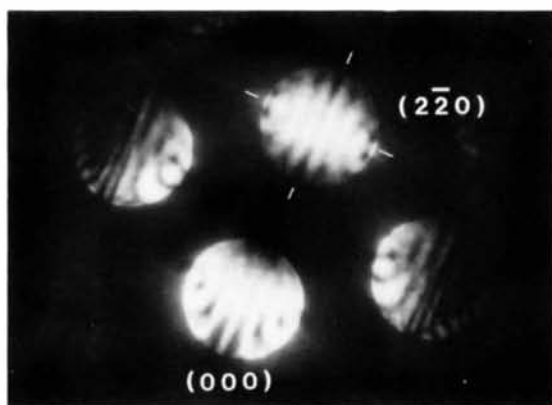


Fig. 5. The internal  $2mm$  symmetry of a  $(220)$  disc in Bragg position from the Au bicrystal of Fig. 3.

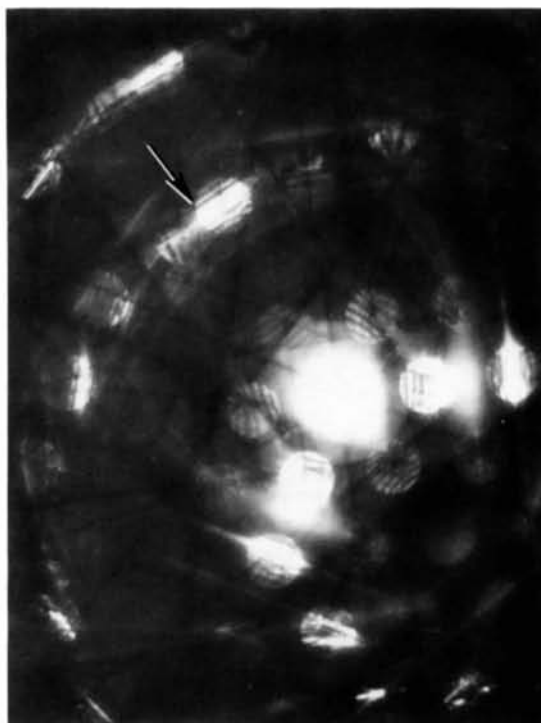


Fig. 6. An off-axis CB pattern from a twinned Au crystal tilted along the 224 Kikuchi band. Note the lack of mirror symmetry between the 551 matrix and twin reflexions arrowed.

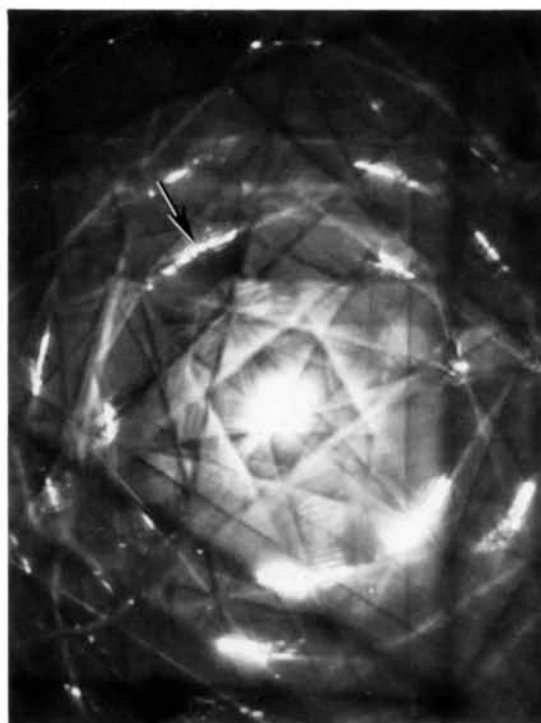


Fig. 7. Off-axis CB pattern as in Fig. 6, but tilted further along the 224 Kikuchi band. Note that the Kikuchi pattern does not have mirror symmetry about the line parallel to  $(220)$ .

CBED pattern by using a specimen with it inclined to the surface and obtaining a series of patterns for different depths of the boundary. Such an investigation will be undertaken in due course. Meanwhile, a useful, although rough, estimate of the relative thickness of the matrix and twinned parts of a bicrystal may be obtained from the spacing of the fringe patterns in symmetrically excited matrix and twin reflexions that are not significantly affected by dynamical diffraction, as shown in Fig. 8. From this pattern, the thicknesses of matrix and twinned parts of the specimen are estimated to be roughly equal.

#### 4. Discussion

The primary aim of this investigation was to explore the possibilities of a symmetry determination of a particular class of bicrystals using CBED. The relationship between the diffraction groups and the dichromatic groups used to describe the symmetry of the crystalline composite was therefore established and a simple case, a (111) coherent twin boundary in a f.c.c. Au crystal examined in detail. The dichromatic point group was found to be  $6'/m'm'm$  from which, by using Table 1 of Schapink & Mertens (1981), it can be concluded that the state of translation at a (111) coherent boundary in Au is either zero or equal to half the lattice spacing of

adjacent (111) planes in the bicrystal. In the latter case, the [111] axis is a screw axis,  $6'_3$ , in the bicrystal but there would be no extinctions due to this axis or its associated  $c'$ -glide plane in our [111] zone-axis patterns. Our results are therefore consistent with the expected state of zero translation but cannot entirely exclude the possibility of a translation of half a lattice spacing parallel to [111]. Our results are also consistent with the assumption that the boundary is ideally located at or near the mid-plane of the bicrystal. The detailed effect of a non-ideal location of the boundary on the pattern has yet to be evaluated and consequently care should be taken in the interpretation of CBED pattern symmetry from bicrystals. Nevertheless, we believe this method to be quite useful for analysing the structure of grain boundaries parallel (or nearly parallel) to the surface of a crystal. A brief comparison of this method with Pond's method of determining translations (Pond & Vitek, 1977) has been presented previously (Schapink & Mertens, 1981).

As has been pointed out in § 2.1, this paper is restricted to grain boundaries occurring in the kind of coincidence-related bicrystals frequently encountered in physical metallurgy, *i.e.* boundaries characterized by a CSL for which  $\Sigma > 1$ . This excludes cases of twinning by merohedry (Friedel, 1926) in which the CSL has the same unit cell as the constituent crystals. This type of twinning may occur in crystal structures having a point group which is a subgroup of the (holohedral) point group of the lattice. Incorporation of such twinning phenomena requires an extension of Table 1 that gives the relationship between the diffraction groups and the dichromatic groups since in these cases the dichromatic groups may contain a coloured inversion centre or belong to the cubic system. All 58 coloured point groups should then have been included in Table 1.

The authors would like to thank Dr R. C. Pond for providing a preprint of his paper with Vlachavas on bicrystallography and for showing one of us (BFB) the use and significance of the dichromatic description of bicrystal symmetry.

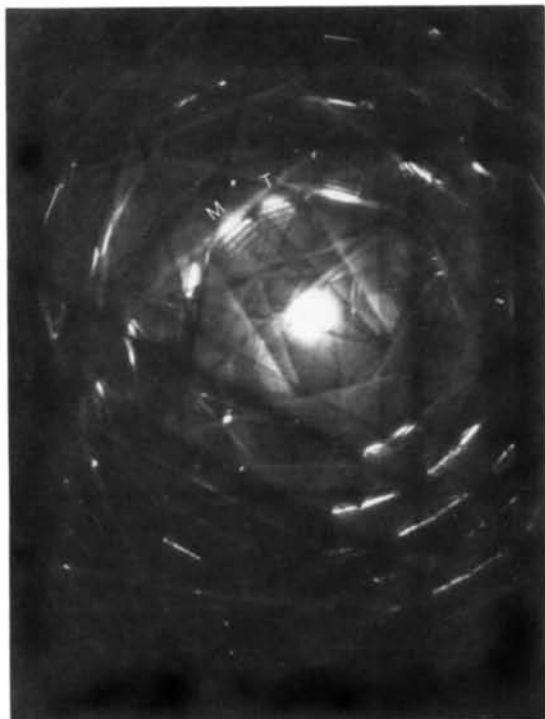


Fig. 8. Fringe pattern in symmetrically excited matrix (*M*) and twin (*T*) reflexions in an off-axis CB pattern tilted along the 224 Kikuchi band.

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## Unbiased Three-Dimensional Refinement of Heavy-Atom Parameters by Correlation of Origin-Removed Patterson Functions

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### Abstract

A procedure is presented for three-dimensional refinement of heavy-atom parameters without the use of phase information in the methods of single and multiple isomorphous replacement. This procedure is based on the Patterson-function correlation method of Rossmann [*Acta Cryst.* (1960), **13**, 221–226] except that the origins of the Patterson functions are now removed from this correlation and centric and acentric reflections are treated separately. The resulting procedure is shown theoretically and by application to three test cases to yield accurate and essentially unbiased estimates of the occupancies, thermal parameters, and positions of heavy-atom sites.

### Introduction

Often a difficult step in the determination of the structure of a crystalline protein by the methods of single or multiple isomorphous replacement (SIR or MIR) is the refinement of positions, occupancies, and thermal factors of the heavy atoms bound in the isomorphous derivatives.

Two general methods have been commonly used to carry out this refinement. The method of Dickerson,

Kendrew & Strandberg (1961) requires several isomorphous derivatives, all of which (Dickerson, Weinzierl & Palmer, 1968) or some of which (Blow & Matthews, 1973) are used to determine approximate phases for the protein structure. These phases are in turn used to refine the heavy-atom parameters for one or more derivatives. In the SIR method, and often during early stages of the MIR method, however, it is necessary to refine the heavy-atom parameters for a single derivative. Since this refinement method requires several derivatives, it cannot be effectively used in these cases. Also, as Blow & Matthews (1973) have pointed out, this method does not yield unbiased estimates of the occupancies of heavy-atom sites.

The least-squares method of Rossmann (1960) and related methods due to Hart (1961) and Kartha (1965) require only a single isomorphous derivative and do not involve the calculation of phases. These procedures are based on the concept that the difference between derivative and native structure-factor amplitudes is related to the true heavy-atom structure-factor amplitude. In the method of Rossmann (1960), heavy-atom parameters are refined so as to minimize the sum over all reflections  $hkl$  of the residual  $R$ :

$$R = \sum_{hkl} \omega^{hkl} [(F_{ph,obs}^{hkl} - F_{p,obs}^{hkl})^2 - (f_{calc}^{hkl})^2], \quad (1)$$

where  $F_{ph,obs}^{hkl}$  and  $F_{p,obs}^{hkl}$  are observed derivative and native structure-factor amplitudes for a reflection with indices  $hkl$ ,  $f_{calc}^{hkl}$  is a heavy-atom structure-factor amplitude calculated from the estimated heavy-atom

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